

NASA Contractor Report 166075

NASA-CR-166075
19830010639

ACETYLENE-TERMINATED POLYIMIDE ADHESIVE

Annemarie O. Hanky

**Kentron Technical Center
Hampton, Virginia 23666**

**Contract NAS1-16000
February 1983**



NF02247



**National Aeronautics and
Space Administration**

**Langley Research Center
Hampton, Virginia 23665**

LIBRARY COPY

MAR 1 - 1983

**LANGLEY RESEARCH CENTER
LIBRARY, NASA
HAMPTON, VIRGINIA**

TABLE OF CONTENTS

		<u>PAGE</u>
1.0	INTRODUCTION	1
2.0	EXPERIMENTAL	2
2.1	Materials	2
2.2	Synthetic Procedure	2
2.2.1	Synthesis of 1N Length of the Imidesulfone	2
2.3	Preparation of Films	3
2.4	Characterization	4
2.5	Adhesive Preparation	4
3.0	RESULTS AND DISCUSSION	5
3.1	Synthesis	5
3.2	Melt-Flow and Cure Properties	6
3.3	Glass Transition Temperature	7
3.4	Thermooxidative Stability	7
3.5	Adhesives	8
3.5.1	Preliminary Screening	8
3.5.2	Processing and Selection	8
3.5.3	Polyimidesulfone Aging	9
4.0	SUMMARY	10
	REFERENCES	11
	TABLES	12
	FIGURES	14

This Page Intentionally Left Blank

FOREWORD

This is a report covering the results of a program designed to develop and characterize an acetylene-terminated, polyimide adhesive for high temperature, aerospace structural applications. This work was accomplished under Contract NAS1-16000 and covers work conducted from July 1981 to May 1982. Customary units were used for reporting the results of this research. Dr. Terry L. St. Clair was Technical Monitor for this project. The work was performed by Annemarie O. Hanky of Kentron International, Incorporated.

The assistance of Mr. James Tyeryar and Mr. Spencer Inge is greatly acknowledged for their help in the bonding and testing of all lap shear specimens in this project. In addition, the assistance of Mr. James Dezern and Mrs. Karen Whitley is also greatly acknowledged for their help in characterization of the oligomer systems.

Use of trade names or names of manufacturers in this report does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

1. INTRODUCTION

During the past decade, a significant effort has been expended on the development of addition curing polyimide systems. The cure mechanism of these systems is such that little or no volatiles are evolved, and these systems usually have high temperature capabilities. LARC-13 (fig. 1) is a nadic-endcapped, addition curing polyimide that exhibits these particular qualities. In addition to its excellent processability, it can be utilized for short periods of time at temperatures up to 593°C. Excellent retention of both initial room temperature (RT) and 316°C lap shear strengths have been achieved after aging in air for up to 125 hours at 316°C. However, bond strength decreases after aging longer than 125 hours at 316°C.¹

An acetylene-terminated addition polyimide was developed at Hughes Aircraft Company under Air Force funding.² It is commercially available under the name Thermid 600*. Thermid 600 has exhibited excellent thermomechanical properties up to 316°C. However, it has a flow time that is quite short, only 100 to 180 seconds.³ Unlike LARC-13, Thermid 600 is difficult to process.

The main purpose of this research was to create a hybrid addition curing polyimide system that retains excellent flow properties while improving the retention of lap shear strength after long-term aging at elevated temperature. To this end, the nadic endcap in LARC-13 was replaced with an acetylene endcap. The use of acetylene endcaps has previously been shown to improve the thermooxidative stability of this addition polyimide system.^{4,5} Also, three different meta-linked, aromatic diamines were screened by substitution into the polymer backbone. Each of these three different systems was prepared at three molecular weights (i.e., three different repeat unit lengths). The screening of these different systems at various molecular weights was done in order to optimize flow properties and adhesive strengths. From this series of tests, the most promising imide oligomer system was selected for aging studies. The results of this study will be discussed.

*Use of trade names or names of manufacturers in this report does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

2. EXPERIMENTAL

2.1 Materials

Commerically available bulk chemicals were used as received. Recrystallized 3,3',4,4' benzophenone tetracarboxylic dianhydride (BTDA) was obtained from King Mar Laboratories, San Diego, California, m.p. 225°C. Glass distilled, N-methylpyrrolidone (NMP) was used as received from Burdick and Jackson, Muskegon, Michigan, b.p. 197-202°C. Aminophenylacetylene (APA), b.p. 106-107°C, was obtained from Gulf Chemicals, Overland Park, Kansas. Diethylene glycol dimethyl ether (diglyme) or 2-methoxyethyl ether was supplied by Aldrich Chemical Company, Milwaukee, Wisconsin, b.p. 162°C. 3,3'-Diaminobenzophenone (DABP), m.p. 151-154°C was prepared by Ash Stevens, Detroit, Michigan. Gulf Research and Development Co., Pittsburg, Pennsylvania, prepared the 3,3' methylenedianiline (MDA), m.p. 79°C. The 3,3' diaminodiphenylsulfone (DDSO₂) was obtained from FIC Corporation, San Francisco, California, m.p. 172-173°C.

2.2 Synthetic Procedure

Three different acetylene-terminated polyimide systems were prepared by varying the diamine present in the chain backbone. The diamines, 3,3' DDSO₂, 3,3' MDA, and 3,3' DABP (fig. 2) were selected for testing because of their meta-linkage. Meta-oriented diamines have been shown to improve the processability and adhesive strength of polyimides as compared to the para isomers.⁶ Each of these polyimides was synthesized and studied at three different molecular weights by varying the stoichiometry so as to achieve a repeat unit chain length of 1, 2, or 3 units (fig. 3). Hereafter, these repeat unit chain lengths will be designated 1N, 2N or 3N. A typical procedure for the synthesis of the imidesulfone oligomer with one repeat unit in the backbone will be presented.

2.2.1 Synthesis of the 1N Length of the Imidesulfone

Using a magnetic stirrer, 0.0542 mole NMP was mixed with 0.0040 mole BTDA in a 50 ml, 3-necked bantamware flask. A mixture of 0.0040 mole of the endcap, APA

and 0.0336 mole of diglyme, were placed in a 10 ml dropping funnel situated in one neck of the flask. Through another neck, 0.0020 mole of 3,3' DDSO₂ was added as a solid. The APA/diglyme mixture and the 3,3' DDSO₂ were then alternately added in five equal portions over a one hour period. This yielded a solution of 20% solids. The reactions were only slightly exothermic, and no heating or cooling was necessary. The time between additions was increased as needed to allow later additions to dissolve in the more concentrated medium. The mixture was stirred until complete solution was obtained, usually overnight. The amic acid resin was precipitated in water, collected, dried in a vacuum oven at 150°C for 30 minutes, and stored in brown glass. A larger volume of this material was made with a higher solids content and stored in amic acid resin form for adhesive testing. This same procedure was used with different stoichiometries to produce the 2N and 3N lengths of this sulfone system. A typical reaction pathway is shown in figure 4. This entire procedure was repeated to generate the 1N, 2N, and 3N chain lengths of the MDA and DABP based systems. Gel permeation chromatography (GPC) analysis was performed on each of the oligomers to determine the relative molecular weight distribution.

2.3 Preparation of Films

Films were cast from the resins to determine the glass transition temperature (T_g) by thermomechanical analysis (TMA) and differential scanning calorimetry (DSC). They were also used to compare the infrared (IR) spectra of the partially cured powders with that of the fully imidized film. Resin (40% solids in a 50/50 mixture of diglyme and NMP) was spread onto a 0.6 cm thick sheet of plate glass using a doctor blade with a 0.0075 cm blade gap. The plate glass was lightly coated with a release agent. The films were air-dried until tack free and staged to 300°C in an air oven according to the following schedule:

<u>Temperature</u>	<u>Hold At Temp</u>
Ambient to 100°C	1 Hour
100°C → 150°C	1 Hour
150°C → 250°C	25 Min.
250°C → 300°C	1 Hour
300°C → ambient oven	Overnight

This schedule yielded films approximately 0.0025 cm thick which were used for the IR spectroscopic analyses.

2.4 Characterization

IR spectra were obtained on both a Nicolet 3600 Fourier Transform Infrared Spectrophotometer (FTIR) and a Perkin-Elmer 297 Infrared Spectrophotometer. A duPont Model 990 Thermal Analyzer/Differential Scanning Calorimeter was used at a programmed heating rate of 20°C/minute to determine T_g, melt-flow properties and cure temperatures of the materials. Apparent T_g of films was determined on a duPont Model 940 TMA at a 5°C/minute heating rate.⁷ Dynamic mechanical analyses were performed on a duPont Model 981 Dynamic Mechanical Analyzer (DMA). Thermooxidative stabilities were measured in static air on a Perkin Elmer Model TGS-2 Thermogravimetric Analysis (TGA) System at a 2.5°C/minute heating rate. Relative molecular weight distribution was determined by gel permeation chromatography using a Waters Associates Model 202/R401 High Pressure Liquid Chromatograph with μ -styragel gradient columns and a refractive index detector. The flow rate was 1.5 ml/min under 2,000 psi pressure using dimethylacetamide (DMAc) as the solvent.

2.5 Adhesive Preparation

An adhesive scrim cloth was prepared for each resin by stretching Type 112-E glass cloth with an A-1100 finish across a 15 cm x 15 cm aluminum frame. The adhesive resins were brush coated onto the cloth. Five to nine applications were required to build up the coatings to the desired thickness of 0.03 cm. After each coat, the cloth was air dried and then staged in a forced air oven to 140°C for 0.5 hour to drive off solvent and begin imidization. The 2.54 cm wide titanium alloy (6 Al-4V) fingers were grit blasted, washed, and treated with Pasa-Jell 107. The titanium adherends were then primed with resin and heated to 140°C for 0.5 hour. The scrim cloth was cut and sandwiched in the 1.27 cm bond line between the two primed adherends. The adherends were then bonded under pressure according to the following cycle:

Apply 50 psi at start, heating rate of 5.0°C/minute:

<u>Temperature</u>	<u>Hold</u>
RT → 225°C	15 Minutes
225°C → 275°C	30 Minutes
275°C → 300°C	No Hold-Cool To Below 100°C Before Removing From Press

Bonded specimens were isothermally aged for 1,000 and 5,000 hours at 177°C with temperatures controlled within $\pm 2\%$ as monitored by a Fluke Datalogger Model 2240C. All lap shear tests were conducted on an Instron Universal Testing Machine according to ASTM D-1002.

The flashing produced from the bonding process was cut from between the titanium fingers and tested for Tg and relative modulus.

3. RESULTS AND DISCUSSION

3.1 Synthesis

Comparison of IR spectra of materials in partially cured and fully cured states show the conversion from amic acid to the imide. The IR of the partially cured powder of the DABP based material with a repeat unit of two is shown in figure 5a. The broad N-H stretch at 3280 cm^{-1} and the amide II band at 1548 cm^{-1} are present. There is also evidence of the conversion from the amic acid to the imide with imide type absorption at 1782 cm^{-1} and 1730 cm^{-1} . An IR of this material as a film fully cured at 300°C for 1 hour appears in figure 5b. The arrows show a complete loss of both the amic acid N-H stretch and the amide II band. The arrows also point out the characteristic imide type bands at 1782 cm^{-1} and 1730 cm^{-1} as well as bands at 1380, 1150 and 720 cm^{-1} , which indicate that cyclization has occurred.

GPC was performed to determine the relative distribution of the molecular weights within each system. Figure 6 shows the GPC of the 1N, 2N and 3N chain lengths of the sulfone system. The elution in the GPC runs from left to right with higher molecular weight fractions eluting first. The figure shows that in the oligomer synthesized to have predominantly one repeat unit in the chain backbone, the low molecular weight fraction to the far right is dominant. As the chain length is increased to two, this low molecular fraction lessens and a higher molecular weight fraction begins to grow. With three repeat units in the chain backbone, the low molecular weight fraction becomes quite small and the middle fraction decreases while a broad higher molecular weight fraction emerges. This trend of increasing molecular weight with increasing chain length indicates the repeat unit chain length was growing as expected, and confirms the synthetic procedure.

3.2 Melt-Flow and Cure Properties

The onset and maximum temperatures of the exotherm in the melt-flow region indicate how fast the functional end group is setting up or crosslinking. The curing exotherm of these acetylene-endcapped systems occurred at sufficiently low temperatures to overlap the melt region. That is, the melt proceeds directly into the cure exotherm without interruption, as shown in figure 7. It should also be noted that the endotherm could be affected by water given off during the curing process.

The melt-cure temperatures of the prepolymers studied are listed in Table 1, which indicates the temperature range of the melt-flow (endotherm) region of the oligomers, as well as the curing (exotherm) region of the material.

The nadic-capped LARC-13 polyimide has an endotherm onset temperature of 160°C.⁵ All acetylene terminated systems studied had comparable melt-onsets. In the sulfone system, the temperature of the melt onset and cure increased with increasing molecular weight or chain length. This system showed the most pronounced stepwise increase in its behavior with catenation. The MDA system showed very small increases in cure temperature in comparison to the sulfone, but still showed a general increase in cure temperature with increased chain length.

All three chain lengths of the MDA system appeared to have the same melt profile. With chain lengths of 1N and 2N, the MDA materials seemed to have two components in the melt onset (fig. 8). This caused the melt onset to be spread over a broader range rather than being sharp. The DABP exhibited this same general increase in its melt and cure profile except in the 3N oligomer (fig. 9). Here the melt onset and minimum temperatures showed a drop instead of increasing with chain length as expected. This parallels a surprising drop in lap shear strength by this same material which will also be discussed later. Also of note, N. Bilow reported a melting point of 210°C for the DABP polyimide.^{2c} This is identical to the melting point reported on our 2N/DABP polyimide system.

3.3 Glass Transition Temperature

The apparent T_g was measured by TMA using cured films and by DMA using the cloth-supported flashing cut from between the titanium fingers after bonding. The T_g data in Table 2 indicates that as the crosslink density increases the T_g increases (i.e., the chain with fewer repeat units and, consequently, shorter distance between crosslinks, has higher T_g value.). Higher molecular weight systems, those with 3 repeat units in the chain backbone, have T_g 's that are comparable to that reported for LARC-13 (repeat unit length of ~ 1.67) whose T_g as a cured polymer is 248°C.⁵

3.4 Thermooxidative Stability

Thermooxidative stability of these acetylene-terminated systems was determined by thermogravimetric analysis. All of the systems, the acetylene-terminated DDSO₂, MDA, and DABP based oligomers had nearly identical thermograms after cure, irrespective of the system or repeat unit length being tested. A typical example, the MDA system with two repeat units in the chain backbone, is shown in figure 10. The broken line indicates the TGA of the nadic-capped LARC-13 which experienced a 50% weight loss at approximately 540°C.⁵ The MDA material exhibited the typical increased thermal stability for all the acetylene-terminated systems, with 50% weight losses occurring between 570°C and 585°C. The LARC-13 also shows rapid weight loss beginning at 177°C. The acetylene-terminated systems show no weight loss below 300°C.

3.5 Adhesives

3.5.1 Preliminary Screening

Results of preliminary lap shear strength (LSS) tests used for screening the three polyimide systems appear in Table 3. The specimens were tested at RT and 177°C and each tabulation is the average of two test specimens. (The range of data about the average is given in parentheses.) These values served to indicate which system held the most promise for long term aging. Essentially, two staging procedures and four bonding pressures were used to try to optimize the LSS of each system.

The scrim cloths initially were taken to 175°C and held for 0.5 hours, and then bonded under 50 psi pressure, applied 15 minutes into the bonding process.

The 1N sulfone system exhibited excellent flow, thin bond lines and good LSS under these conditions. The LSS showed a dramatic increase at the higher 177°C test temperature compared to the room temperature test.

The MDA material had 50% thicker bond lines than the sulfone, lower LSS with much larger scatter and a much smaller increase in LSS at the higher test temperature. Finally, the 1N/DABP system gave a bond so weak it broke upon removal from the press.

3.5.2 Processing and Selection

The data described in the preceeding section indicated that the MDA and DABP systems were setting up too quickly to retain the necessary flow for bonding. Therefore, the next scrim cloths were coated and staged only to 140°C for 0.5 hour. The bonding pressure was applied from the beginning in all of the remaining bonding processes.

With these adjustments, the bond process was repeated on the 2N specimens from each system. Again the sulfone system had the highest LSS and the largest increase in LSS at higher test temperature. It had slightly thinner bond lines but there was also more scatter in these samples than in the 1N samples. The 2N/MDA at RT

had low LSS; however, the LSS at 177°C showed a substantial increase. The scatter was very large. The 2N/DABP system did bond this time; however, the bond line was very thick and the LSS's at RT and 177°C were only moderate in comparison to the DDSO₂ LSS.

The 3N scrim cloths for each of the systems were also staged to 140°C in an effort to obtain more flow. The sulfone again showed an increase in its LSS over the previous systems with thin bond lines and moderate scatter. 3N/MDA and 3N/DABP systems were bonded under high pressure in an effort to improve their bond strength, but this yielded LSS that were low and highly variable.

With the screening procedures completed, the DDSO₂-based system was selected for further aging studies because it had exhibited obvious advantages over the MDA or DABP systems. It had superior flow at low bonding pressure and the highest LSS, which increased with temperature and repeat unit length. Also of note, the DDSO₂ diamine was the least expensive of the three diamines making it the more attractive choice from an economic standpoint.

3.5.3 Polyimidesulfone Aging

Each of the three chain lengths of the sulfone system was prepared in larger batches. Lap shear test specimens were prepared, and, this time, four test specimens were averaged for each data point. Initial values were obtained at RT and 177°C for each oligomer. The remaining specimens were aged for 1,000 hours and 5,000 hours at 177°C.

Table 4 shows LSS's of the aged specimens after 1,000 hours. Examination of the results for the aged specimens tested at elevated temperature shows the DDSO₂ material lost an average of only 11% of its initial lap shear strength. The highest percentage loss was for the 2N system at 16%. Aging is continuing on these materials.

4. SUMMARY

A group of acetylene terminated polyimides was synthesized to study the effects of chemical modifications on a LARC-13 type backbone. The three acetylene-endcapped materials were selected for screening in an effort to develop a system that has better retention of lap shear strength after aging than LARC-13 with similar processability. All acetylene systems were identical in structure except for the variation in the meta-linked diamine. These diamines were diaminodiphenylsulfone (DDSO₂), methylenedianiline (MDA), and diaminobenzophenone (DABP).

The DDSO₂ or sulfone material gave the highest lap shear strengths (LSS) of the three systems and also yielded thinner adhesive bond lines and exhibited good flow properties. The MDA and DABP systems had poor flow and thick bond lines. These two systems showed no encouraging improvements of LSS with changes in repeat unit length or test temperature. The sulfone system exhibited an increase in LSS at the higher test temperature, thereby showing potential as a system suitable for long term use at 177°C. The sulfone monomer is commercially available and also the least expensive of the three diamines. For these reasons, the sulfone was chosen for further study in an aging program of 1,000 hours and 5,000 hours at 177°C. After 1,000 hours at 177°C, the sulfone lost an average of only 11% in LSS when tested at 177°C. The 5,000 hours aging program for these systems is still in progress.

REFERENCES

1. T. L. St. Clair and D. J. Progar: LARC-13 Polyimide Adhesive Bonding. SAMPE Sym. Proceedings; 24 (2), 1081 (1979).
2. a. N. Bilow, A. L. Landis, and L. J. Miller: Acetylene Substituted Polyamide Oligomers. U.S. Patent 3,845,018, October 29, 1974.
b. N. Bilow, A. L. Landis: Homopolymerization of Acetylene Substituted Polyimide Polymers. U.S. Patent 3,879,349, April 22, 1975.
c. N. Bilow, et al: New Developments In Acetylene-Substituted Polyimides. SAMPE Sym. Proceedings, 23, 791 (1978).
d. N. Bilow, et al: Acetylene-Substituted Polyimide Adhesives. SAMPE Journal, 18 (1), 8 (1982).
3. R. J. Kuhbander and T. J. Aponyi: Thermid 600 Adhesive Formulation Studies. SAMPE Tech. Conf. Proceedings, 11, 295 (1979).
4. T. L. St. Clair: Addition Polyimide End Cap Study. NASA TM-81917, 1980.
5. A. K. St. Clair and T. L. St. Clair: Addition Polyimide Adhesives Containing Various End Groups. Polymer Eng. and Sci., 22 (9), 9 (1982).
6. A. K. St. Clair and T. L. St. Clair: Structure-Property Relationships of Isomeric Addition Polyimides Containing Nadimide End Groups. Polymer Eng. and Sci., 16 (5), 314 (1976).
7. Harold D. Burks: Thermomechanical Determination of T_g Using A Modified Film Sample-Mounting Method. J. Appl. Polym. Sci., 18, 627 (1974).

TABLE 1. THERMAL PROPERTIES OF ACETYLENE-TERMINATED POLYIMIDE SYSTEMS.

X-GROUP	n	ENDOTHERM ONSET °C	ENDOTHERM MINIMUM °C	EXOTHERM MAXIMUM °C
$\begin{array}{c} \text{O} \\ \\ -\text{S}- \\ \\ \text{O} \end{array}$	1	165	195	271
	2	168	198	284
	3	181	211	298
$\begin{array}{c} \text{H} \\ \\ -\text{C}- \\ \\ \text{H} \end{array}$	1	149-160	191	270
	2	146-152	190	276
	3	156	190	281
$\begin{array}{c} \text{O} \\ \\ -\text{C}- \end{array}$	1	166	193	266
	2	181	210	278
	3	156	194	290

TABLE 2. APPARENT GLASS TRANSITION TEMPERATURE (T_g) BY DYNAMIC MECHANICAL ANALYSIS OF ACETYLENE-TERMINATED POLYIMIDE SYSTEMS.

DIAMINE	REPEAT UNIT	T_g APPARENT °C (DMA)
DDSO ₂	1	305
	2	284
	3	253
MDA	1	316
	2	279
	3	262
DABP	1	314
	2	292
	3	273

TABLE 3. OPTIMIZATION OF BONDING CONDITIONS FOR SCREENING ACETYLENE-TERMINATED POLYIMIDE SYSTEMS.

SAMPLE	BONDING PRESSURE, psi	AVG BOND THICKNESS, mm	AVG LSS AT RT, psi (RANGE)	AVG LSS AT 177°C, psi (RANGE)
3, 3' DDSO ₂				
1N*	50	0 12	2165 (40)	2965 (10)
2N	50	0 10	2885 (110)	3248 (125)
3N	50	0 13	3250 (200)	3200 (150)
3, 3' MDA				
1N	50 200	0 26 0 20	1708 (315) 2245 (200)	1815 (90) 2425 (100)
2N	50 100	0 20 0 50	1613 (75) 1705* (-)	2388 (1525) 2603 (935)
3N	200	0 52	1940* (-)	1498 (955)
3 3' DABP				
1N	50 400	- 0 18	NO BOND 1943 (115)	NO BOND 2165 (630)
2N	50 100	0 34 0 31	1710 (120) 1553 (205)	2003 (125) 2400 (900)
3N	400	0 53	1503 (905)	1333 (45)

*N- REPEAT UNIT LENGTH

*BROKE ON CUTTING - ONLY ONE SAMPLE TESTED

TABLE 4. LAP SHEAR STRENGTH OF ACETYLENE-TERMINATED POLYIMIDE SULFONE AFTER 1,000 HRS. AT 177°C.

REPEAT UNIT	INITIAL LSS, psi		AFTER 1000 HOURS AT 177°C, psi	
	RT	177°C	RT	177°C
1	2219	2872	2024	2565
2	3209	3544	2465	2966
3	3453	3615	2766	3404

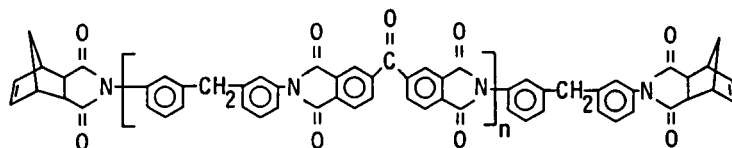


Figure 1. LARC-13 structure.

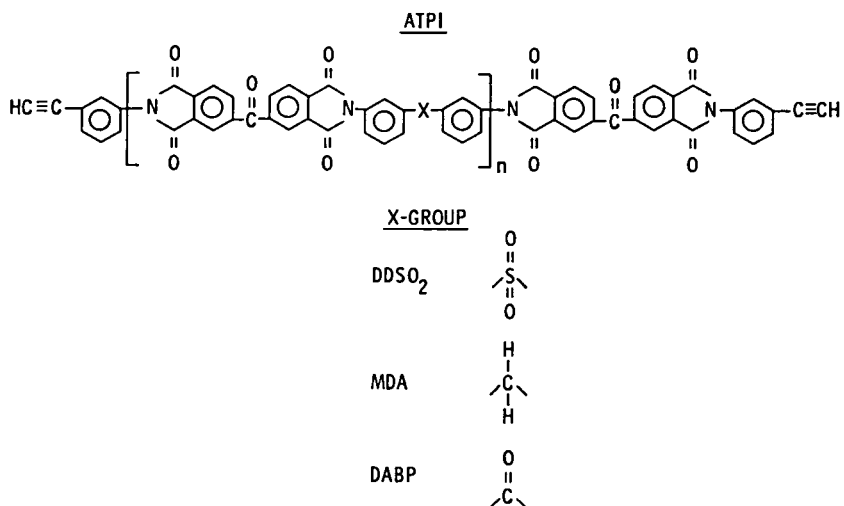


Figure 2. Different structures of acetylene-terminated polyimide systems.

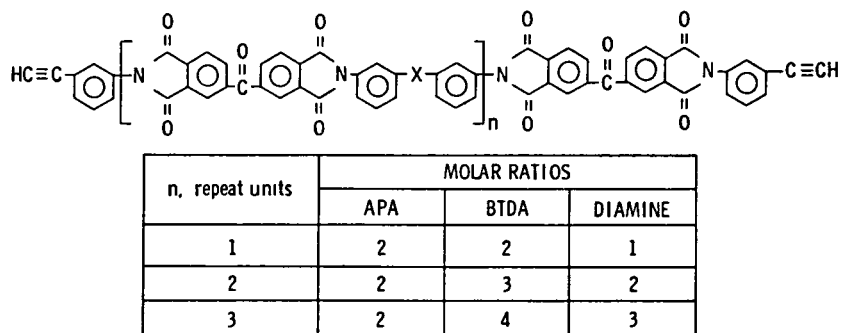


Figure 3. Stoichiometry of different repeat unit lengths.

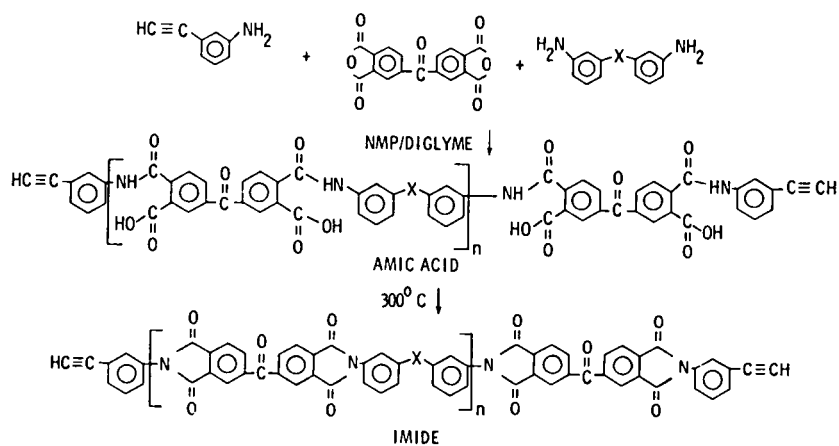


Figure 4. Reaction pathway for synthesis of acetylene-terminated polyimide systems.

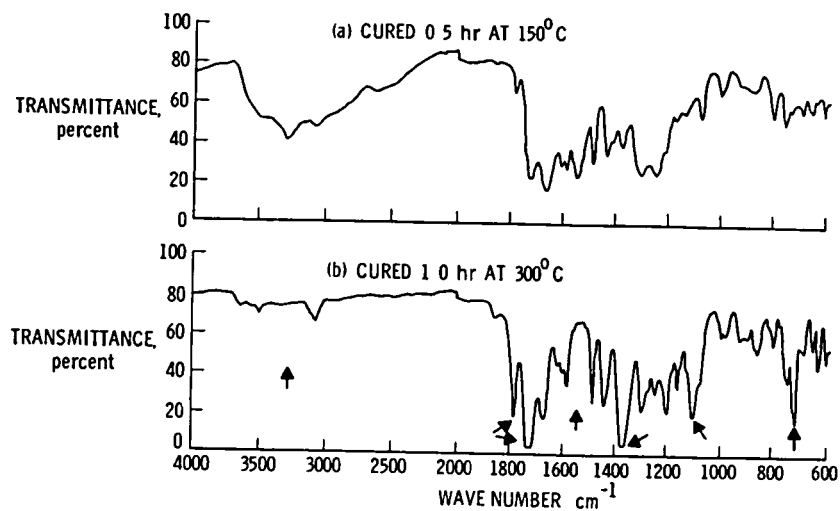


Figure 5. Infrared spectra of 2N/DABP for two cure conditions.

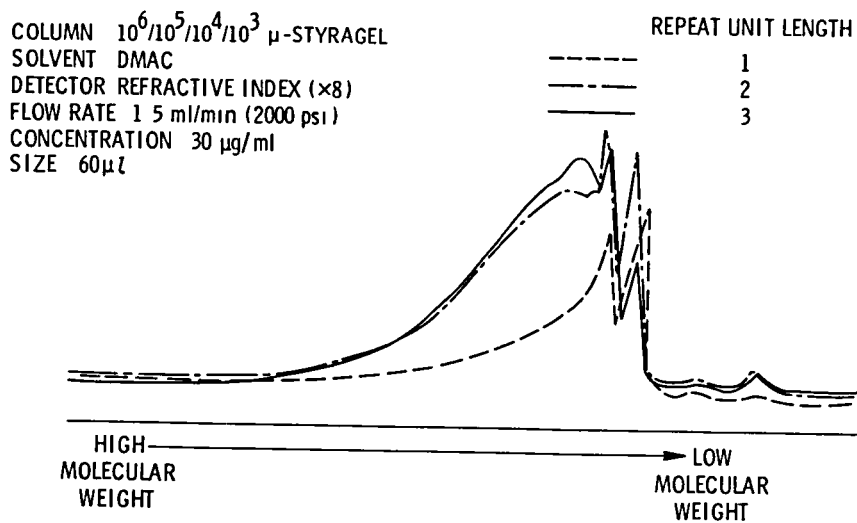


Figure 6. Gel permeation chromatograms of the acetylene-terminated sulfone systems.

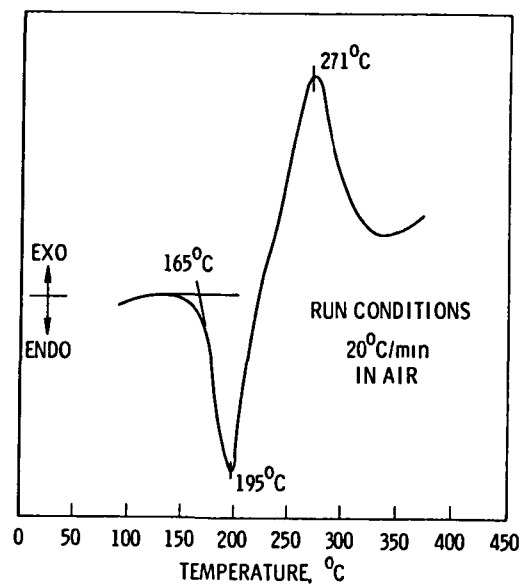


Figure 7. Differential scanning calorimeter thermogram of 1N/DDS₀₂ cured for 0.5 hr. at 150°C.

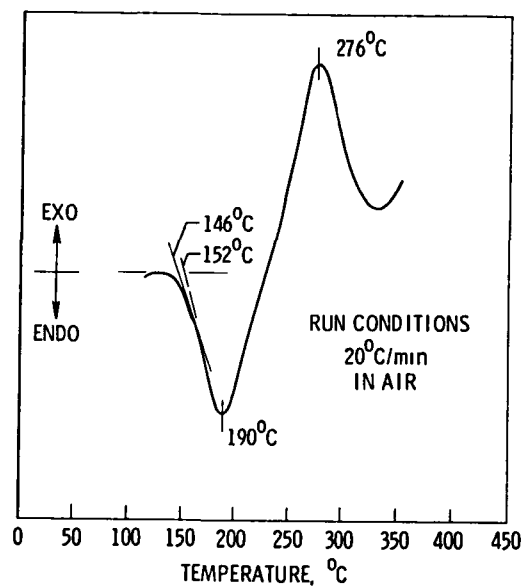


Figure 8. Differential scanning calorimeter thermogram of 2N/MDA cured for 0.5 hr. at 150°C.

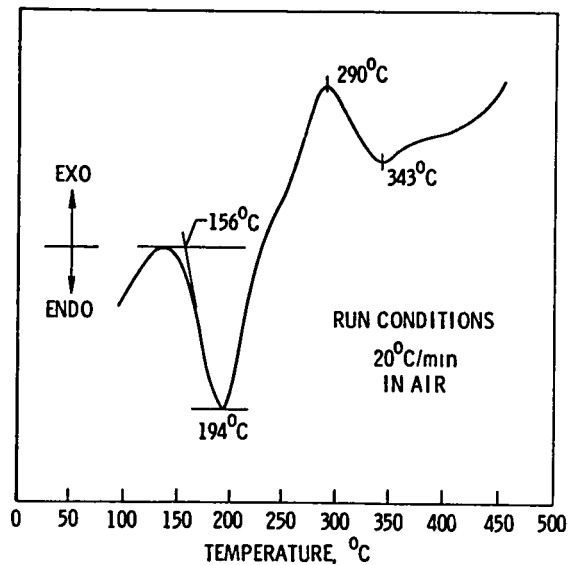


Figure 9. Differential scanning calorimeter thermogram of 3N/DABP cured for 0.5 hr. at 150°C.

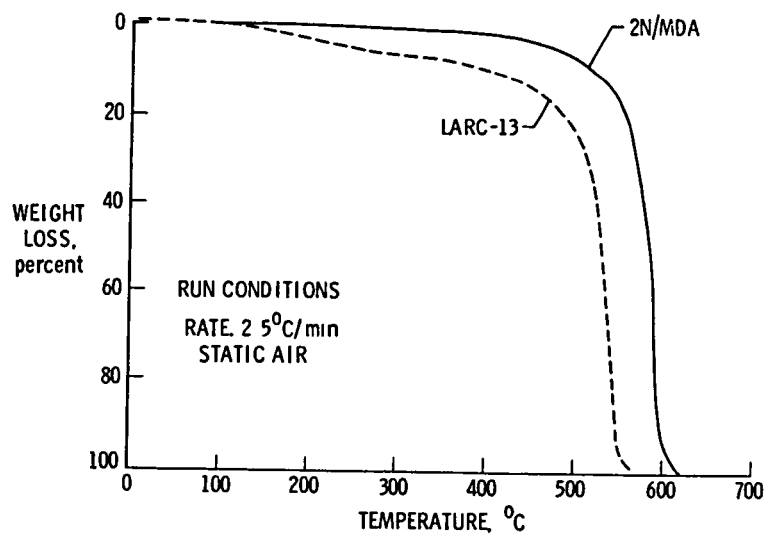


Figure 10. Comparison of thermoxidative stabilities of LARC-13 and a typical acetylene-terminated polyimide system.

1. Report No. NASA CR-166075		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Acetylene-Terminated Polyimide Adhesives				5. Report Date February 1983	
				6. Performing Organization Code	
7. Author(s) Annemarie O. Hanky				8. Performing Organization Report No.	
9. Performing Organization Name and Address Kentron International, Inc. 3221 North Armistead Avenue Hampton, VA 23666				10. Work Unit No.	
				11. Contract or Grant No. NAS1-16000	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546				13. Type of Report and Period Covered Contractor Report 7/81 - 5/82	
				14. Sponsoring Agency Code	
15. Supplementary Notes Langley Technical Monitor: Dr. Terry L. St. Clair					
16. Abstract <p>Over the last decade, a significant amount of research has been reported on addition curing polyimide systems. The cure mechanism of these systems is such that no volatiles are generated and these types of systems usually have high temperature capabilities because of their high crosslink densities and chemical structures.</p> <p>LARC-13 is a nadic-endcapped, addition polyimide that exhibits excellent flow, is easy to process, and can be utilized for short terms at temperatures up to 593°C. It retains good lap shear strength as an adhesive for titanium after aging in air up to 125 hours at 316°C, but lap shear strength degrades with longer exposures at that temperature.</p> <p>Thermid 600 is an addition polyimide that is acetylene endcapped. It exhibits excellent thermomechanical properties even after long term exposure in air at 316°C. An inherent drawback of this system is that it has a narrow processing window.</p> <p>An novel acetylene-endcapped, addition polyimide which is a hybrid of these two systems has been developed. It has good retention of strength after long term aging and is easily processed. The synthesis and characterization of various molecular weight oligomers of this system will be discussed as well as the bonding, aging and testing of lap shear adhesive samples.</p>					
17. Key Words (Suggested by Author(s)) Polyimides Acetylene-Terminated High-Temperature Adhesives 3,3' Diaminodiphenyl Sulfone			18. Distribution Statement Unclassified-Unlimited Subject Category 27		
19. Security Classif (of this report) Unclassified	20. Security Classif (of this page) Unclassified	21. No. of Pages 23	22. Price A02		

End of Document